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(54) **Dentifrice composition containing zeolite**

(57) A dentifrice composition which contains a synthetic zeolite polishing and cleaning agent having an average crystal size of less than about 1 micron and containing less than about 10 percent of crystals greater than about 1 micron in size is disclosed.

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SPECIFICATION

Dentifrice compositions

This invention relates to dentifrice compositions containing a synthetic zeolite as a polishing and cleaning agent.

In order to accomplish the removal of stains, pellicle film, and food debris from the teeth, dentifrice compositions generally contain solid abrasive particles as a polishing and cleaning agent in a suitable carrier. The agent must be abrasive enough to polish and clean effectively but not so abrasive that it damages the teeth by causing scratching or excessive localized abrasion of enamel or dentine surfaces.

Conventional dentifrice abrasives generally include crystalline materials such as calcium pyrophosphate, sodium metaphosphate, calcium carbonate, and calcined alumina and amorphous materials such as silica gel, precipitated silica, silica-alumina gel, and metal aluminosilicate complex salts. These abrasives generally have a weight median particle diameter of from about 2 to about 20 microns but also have broad particle size distributions in which a substantial proportion of the particles have a diameter of greater than about 20 microns. An abrasive containing particles of above about 40 microns in size can be felt organoleptically by the dentifrice user and particles of over about 20 microns in size may scratch or cause undue localized abrasion of the teeth. When these abrasives are further reduced in size to avoid these effects, their cleaning ability is significantly lowered.

U.S Patent No. 4,209,504 discloses an aqueous-based toothpaste containing at least 15 and at most 60 weight percent of an alkali aluminum silicate zeolite as the polishing agent base. The preferred average particle size of the zeolite is between about 1 and 30 microns. The patent teaches that the toothpaste is non-corrosive to aluminum containers, polishes well without excess abrasion, and is compatible with dental fluorine compounds.

In accordance with this invention, it has been unexpectedly found that a dentifrice composition which comprises dental carrier and a synthetic zeolite having an average crystal size of less than about 1 micron and containing less than about 10 percent of crystals greater than about 1 micron in size has the unique characteristics of being able to remove stains from teeth without abrading the enamel or dentine surfaces. The high abrasivity of prior zeolite polishing and cleaning agents may cause undue abrasion of enamel and dentine surfaces. Because of the crystalline hardness and small uniform size of the synthetic zeolites used in the present invention, their abrasiveness is low enough to eliminate undue abrasion, yet sufficiently high for good cleaning and polishing to remove stained pellicle layers from tooth surfaces. Preferably, the zeolite is a filter cake having a water content of at least about 30 weight percent. The use of a filter cake avoids the agglomeration of crystals into larger sizes that occurs on drying and reduces the manufacturing costs of the zeolite for use in the present invention. The zeolites used in this invention also have good fluoride compatibility and do not discolor the dentifrice or impair its flavor.

The synthetic zeolites used in the present invention are crystalline metal aluminosilicates in which the metal may be an alkali metal, an alkaline earth metal, zinc, copper, or a mixture of these metals. Alkali metal zeolites, especially sodium zeolites, are preferred. Other cations, e.g., hydrogen, rare earth or ammonium ions, can be introduced into the zeolite by exchange. These zeolites have the general formula $x(M{\cdot}AlO_2){\cdot}ySiO_2{\cdot}zH_2O$ in which M is the cation, x is a number between 1 and 64, y is equal to nx wherein n is a number between 1 and 6, and z is a number between 0 and about 50.

The zeolites used in the present invention have an average crystal size of less than about 1, preferably less than about 0·8, and especially from about 0·1 to about 0·7 micron. The zeolites contain less than about 10, preferably less than about 5, and especially less than about 1 percent of crystals greater than about 1 micron in size. The average crystal size and crystal size distribution are determined from photographs made in a scanning electron microscope of the zeolites after drying to a water content of about 1 to 3 weight percent and breaking up agglomerates with a mortar and pestle. A sufficient number of crystals, for example 100, is counted and their size measured to determine a statistically significant average (arithmetical mean) size and percentage of crystals of a size greater than 1 micron. The photographs show individual crystals and some interconnections between crystals which would be easily broken by the dispersion employed in preparing the dentifrice.

The zeolites may be in the form of a conventionally dried powder having a water content of from about 10 to about 25 weight percent. Preferably, the zeolite is a filter cake having a water content of at least about 30 weight percent and especially of from about 35 to about 65 weight percent. The zeolite water content is determined as loss in weight after heating for 1 hour at 1750°F. (955°C.). The zeolite may be readily dehydrated to remove substantially all the water to provide an anhydrous zeolite for use in an anhydrous dentifrice by heating it in air or a vacuum at temperatures up to about 600°C.

Preferred zeolites for use in the present invention have a cubic or rounded cubic crystalline symmetry and include type A zeolites and type Y zeolites. Type A zeolites have the chemical composition $[Na_{12}(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$, a cubic crystalline symmetry, a unit cell dimension (calculated for dehydrated zeolite) of about 12·5 angstroms, and a pore size of from 3 to 5 angstroms. Type Y zeolites have the chemical composition $[Na_6(AlO_2)_6(SiO_2)_{10}]\cdot 24H_2O$, a cubic crystalline symmetry, a unit cell dimension (calculated for dehydrated zeolite) of about 25 angstroms, and a pore size of from 8 to 12 angstroms. The type Y and type A zeolites provide dentifrices of especially suitable abrasiveness, color, and flavor. Sodium type Y zeolites are especially preferred because of their superior fluoride and flavor compatibility and stability and desirable abrasiveness.

Commercially available synthetic zeolites are suitable for use as the polishing agent in the present dentifrice compositions. A particularly preferred zeolite is sodium 13Y zeolite. Such a product is sold by the Davison Chemical Division of W. R. Grace & Co., Baltimore, Maryland, U.S.A. in the form of a powder as molecular sieve Grade C551 and has an average crystal size of 0·6 microns, less than 1 percent of crystals greater than 1 micron in size, a water content of 17·5 to 24·9 weight percent, and a pH of 10·0 to 10·8. The product sold as Davison Grade 550 has the same properties except that it is in the form of a filter cake having a water content of 60 weight percent. Another particularly preferred zeolite is sodium zeolite 4A which is sold in the form of a powder as Davison molecular sieve Grade C515. The C515 product has an average crystal size of 0·7 microns, less than 1 percent of crystals greater than 1 micron in size, a water content of 20 weight percent, and a pH of 11·3.

The preparation and properties of zeolites having the small uniform crystal size suitable for the present invention are described in Breck, *Zeolite Molecular Sieves*, pp. 245–378 (1974). The crystal size of the zeolite is controlled by the synthesis temperature and time. Generally, zeolites having an average crystal size and crystal size distribution suitable for this invention may be obtained by conducting the synthesis at temperatures of from about 25 to about 100°C. for periods of from about 4 hours to about 7 days. Lower temperatures and times within these ranges produce lower average sizes and fewer oversize particles.

The zeolite abrasives used in the present invention provide highly effective cleaning and polishing of teeth as measured by their radioactive dentine abrasion (RDA) values. The RDA values are determined in accordance with the procedure of the American Dental Association described in Hefferman, *J, Dent. Res.*, pp. 563–573 (July–August, 1976) with the following exceptions. The RDA values are determined using a slurry containing 6·25 grams of the zeolite instead of the 10·0 grams of the abrasive powder used in the American Dental Association procedure. The amount of zeolite powder or filter cake used in the slurry is determined on the basis of a water content of 20 weight percent. Also, the RDA values throughout the specification are based on an RDA value of 500 for the calcium pyrophosphate reference standard instead of the value of 100 assigned to this reference standard in the American Dental Association procedure. The zeolites of this invention generally have an RDA value of at least about 200 and preferably have an RDA of at least about 300. Typically, the RDA of the zeolite used in this invention ranges from about 400 to about 700.

The dentifrice compositions of this invention comprise a dental carrier and a polishing and cleaning effective amount of the zeolite abrasive. The compositions may be used as prophylactic dental creams or pastes applied by a dentist or dental technician in polishing of teeth after removal of calculus deposits, in preparations for use on dentures, and in toothpastes and toothpowders for daily use on the teeth. The zeolite generally comprises from about 5 to about 50 percent and the dental carrier from about 50 to about 95 percent by weight of the dentifrice composition. Preferably, the zeolite comprises from about 5 to 35 weight percent and the dental carrier from about 65 to about 95 weight percent. The dental carrier is orally acceptable, i.e., suitable for use on teeth and dentures and for introduction into the oral cavity without significant adverse effect on tooth structure or other injury to health.

Dentifrices can be prepared in various physical forms including paste, powder, liquid, and tablet. The dental carrier for any form of dentifrice generally comprises a soap or synthetic surface-active agent to assist in dispersing and cleaning and to render the compositions more cosmetically acceptable. The dentifrice compositions of this invention are usually in the form of toothpastes or toothpowders and toothpaste is a preferred embodiment of this invention. In addition to the zeolite abrasive and soap or surface-active agent, toothpowders or dental tablets generally contain flavoring oils and sweetening agents. To make toothpastes or dental creams, the zeolite abrasive is dispersed in a liquid dental vehicle which comprises water, a humectant, or mixtures thereof. Humectants are frequently included to provide smooth texture and flowability and it is usually advantageous to use a mixture of water and one or two humectants. Toothpastes also generally contain a binder and a preservative.

Any organic surface-active agent conventionally used in the dentifrice art may be combined with the zeolite abrasive. The agent may be anionic, cationic, amphoteric, or non-ionic and is preferably a detersive surface-active agent. Water soluble salts of higher (C_{10-20}) alkyl sulfates are

especially useful and the most common agent is sodium lauryl sulfate. The surface-active agent generally comprises from about 0·5 to about 10 per cent and preferably about 1 to about 5 per cent by weight of a toothpaste.

The liquid vehicle of a paste dentifrice usually comprises from about 10 to about 90 weight percent of the composition and from 65 to about 85 weight percent of the vehicle is most commonly employed. The vehicle may include humectants such as glycerine, sorbitol, xylitol, propylene glycol, or polyethylene glycol. Glycerine, sorbitol, and mixtures thereof with water are commonly employed. Typically, the vehicle contains from about 20 to about 80 weight percent of the humectant and about 80 to about 20 percent water.

The toothpastes also generally include one or more thickening, gelling, or binding agents that, along with the abrasive, form the solid phase of the carrier. Any such agents that are compatible with the zeolite abrasives as well as with the other dentifrice components may be used. Suitable agents include, for example, natural and synthetic gums such as Irish moss, gum tracaganth, xanthan gums, hydroxy ethylcellulose, or alkali metal derivatives of carboxymethylcellulose and inorganic materials such as silica aerogels, precipitated silicas, pyrogenic silicas, and natural and synthetic complex silicate clays. The agent is typically present in an amount of up to about 20 percent and preferably comprises from about 0·1 to about 10 percent by weight of the composition.

A minor amount of an additional dentally-acceptable abrasive may also be included in the dentifrice. Suitable additional polishing and cleaning agents include dicalcium phosphate; tricalcium phosphate; insoluble sodium metaphosphate; aluminum hydroxide; calcined alumina; magnesium carbonate; calcium carbonate; calcium pyrophosphate; bentonite; amorphous alkali metal, alkaline earth metal, or ammonium aluminosilicates; crystalline silicas; precipitated silicas; and silica-alumina or silica-magnesia xerogels or hydrogels. Preferred abrasives are silica xerogels, hydrous silica gels, and silica hydrogels because of their superior fluoride compatibility and flavor release. Such additional polishing agents have a weight median particle diameter of from about 2 to 20 microns, and are generally used in an amount of up to about 20 and preferably up to about 10 percent by weight of the dentifrice.

Various other conventional additives may be incorporated in the dentifrice composition of this invention. These additives may be flavoring agents such as the essential flavoring oils; sweetening agents such as sodium cyclamate or saccharin; preservatives such as benzoic acid, chloroform, or sodium benzoate; whitening or coloring agents; anti-bacterial agents such as guanidines, biguanides, or amines; fluorine-containing compounds; anti-plaque additives such as zinc citrate or 8-hydroxy quinoline; anti-corrosive agents such as sodium silicate; and pH adjusters such as citric acid. These additives are generally present in amounts of up to about 10 percent and typically from about 0·1 to about 5 percent by weight of the composition.

The dentifrice may be prepared by combining the ingredients in a conventional manner. A toothpowder is usually prepared by milling the solid ingredients in the appropriate quantities and particle sizes. In making a toothpaste, a gelling agent such as sodium carboxymethyl cellulose, a thickening agent such as silica aerogel, and a preservative such as sodium benzoate, if employed, is dispersed with a humectant such as glycerine. Water may also be present. Additional humectant and water, as an aqueous 70% sorbitol solution, may then be mixed with the dispersion and a paste, gel or cream is formed. Dental abrasive agent, surface-active agent, sweetener, and flavoring are then added. The toothpaste is then thoroughly deaerated and packaged. Dental tablets may be prepared by blending the flavor and a high molecular weight humectant, such as polyethylene glycol, with proportions of the other solid and liquid ingredients as in a toothpaste and forming by conventional methods.

A preferred dentifrice composition of this invention comprises from about 15 to about 35 weight percent of the zeolite abrasive in the form of a filter cake and from about 65 to about 85 weight percent of a liquid dental vehicle comprising a humectant and water.

The following examples further illustrate the invention. All parts and percentages in the examples are by weight unless otherwise indicated.

EXAMPLES 1–3

A variety of synthetic zeolites which are commercially available from Davison Chemical Division, W. R. Grace & Co., Baltimore, Maryland, and have less than 1 percent of crystals greater than 1 micron in size was evaluated for abrasivity. The results and the properties of the zeolites are shown in Table I.

Table I

Example No.	Type	Form	Davison Grade	Average Crystal Size (microns)	Analyses (dry basis)					
					RDA	%H_2O	%Na_2O	%Al_2O_3	%SiO_2	pH
1	4A	Powder	C515	0.7	465	20.0	20.6	35.4	41.4	11.3
2	13Y	Powder	C551	0.6	640	17.5	11.0	21.5	64.4	10.2
3	13Y	Cake	C550	0.6	550	60.0	11.0	21.5	64.4	10.2

The corresponding data for zeolites having an average crystal size greater than 1 micron and containing more than 10 percent of crystals greater than 1 micron in size are shown in Table II for purposes of comparison.

Table II

Comparative Example	Type	Form	Davison Grade	Average Crystal Size (microns)	% of Crystals >1 micron	RDA	% H_2O	% Na_2O	% Al_2O_3	% SiO_2	pH
A	4A	Powder	Sylosiv™100	1.8	>60	850	20.9	21.3	34.6	41.0	11.5
B	13X	Powder	C540	2.7	>80	970	19.6	17.8	32.3	47.2	11.2
C	13X	Cake	C540	2.7	>80	860	46.0	17.8	32.3	47.2	11.2

The radioactive dentine abrasion values of from 465 to 640 of Examples 1–3 and of 850 and higher for the larger zeolites of Comparative Examples A–C demonstrate that the zeolites used in the present invention have an unexpectedly high abrasivity for good cleaning but will not cause any scratching because of the very small uniform crystal sizes.

A dentifrice composition of this invention may be prepared by combining the following ingredients by conventional methods as described above in the following proportions.

Ingredient	*Weight Percent*
Synthetic zeolite filter cake of Example 3	24
Aqueous 70% sorbitol solution	53
Glycerin	10
Silica aerogel	5
Sodium carboxymethylcellulose	0·5
Saccharin	0·2
Flavor	0·5
Sodium lauryl sulfate	1·3
Water and sufficient citric acid to give a final pH of 7·5	5·5

CLAIMS

1. A dentifrice composition comprising a dental carrier and an amount effective for tooth polishing and cleaning of a synthetic zeolite having an average crystal size of less than about 1 micron and containing less than about 10 percent of crystals greater than about 1 micron in size.

2. A dentifrice composition according to claim 1 in which the zeolite has an average crystal size of less than about 0·8 micron.

3. A dentifrice composition according to claim 1 in which the zeolite has an average crystal size of from about 0·1 to about 0·7 micron and contains less than about 5 percent of crystals greater than about 1 micron in size.

4. A dentifrice composition according toclaim 1, 2 or 3 in which the zeolite contains less than about 1 percent of crystals greater than about 1 micron in size.

5. A dentifrice composition according to any of claims 1 to 4 in which the zeolite has a cubic crystalline symmetry.

6. A dentifrice composition according to any of claim 1 to 5 in which the zeolite is a sodium zeolite.

7. A dentifrice composition according to claim 6 in which the zeolite is a Type A zeolite.

8. A dentifrice composition according to claim 6 in which the zeolite is a Type Y zeolite.

9. A dentifrice composition according to any of claims 1 to 8 in which the zeolite has a radioactive dentine abrasion value of at least about 200.

10. A dentifrice composition according to claim 9 in which the zeolite has a radioactive dentine abrasion value of at least about 300.

11. A dentifrice composition according to claim 9 in which the zeolite has a radioactive dentine abrasion value of from about 400 to about 700.

12. A dentifrice composition according to any of claims 1 to 11 comprising from about 5 to about 50 percent of the zeolite and from about 50 to about 95 percent by weight of the dental carrier based on the total weight of the composition.

13. A dentifrice composition according to claim 12 in which the zeolite comprises from about 5 to about 35 percent and the dental carrier from about 65 to about 95 percent by weight of the dentifrice composition.

14. A dentifrice composition according to any of claims 1 to 13 in which the zeolite is included in the form of a filter cake having a water content of at least about 30 weight percent.

15. A dentifrice composition according to claim 14 in which the filter cake has a water content of from about 35 to about 65 weight percent.

16. A dentifrice composition according to any of claims 1 to 15 in which the dental carrier comprises a liquid vehicle comprising water, a humectant, or a mixture thereof.

17. A dentifrice composition comprising from about 15 to about 35 weight percent of a sodium Type Y synthetic zeolite filter cake having a water content of from about 35 to about 65 weight percent and an average crystal size of less than about 0·8 microns and from about 65 to about 85 percent of a liquid dental vehicle comprising a humectant and water.

18. A dentifrice composition according to claim 17 in which the zeolite contains less than about 10 percent of crystals greater than about 1 micron in size.

19. A dentifrice composition according to claim 18 in which the zeolite contains less than about 5 percent of crystals greater than about 1 micron in size.

20. A dentifrice composition according to claim 17 in which the zeolite has an average crystal size of from about 0·1 to about 0·7 micron and contains less than about 1 percent of crystals greater than about 1 micron in size.

21. A dentifrice composition according to claim 1 substantially as hereinbefore described.

22. A synthetic zeolite having an average crystal size of less than 1 micron and containing less than about 10 percent of crystals greater than about 1 micron in size for use in a dentifrice composition as a tooth polisher and cleaner.

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